Magnetoelastic tetragonal-to-orthorhombic distortion in $ErNi_2B_2C$

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We have performed synchrotron x-ray scattering experiments on single crystals of $ErNi_2B_2C$. Below 6.3 K, the (2,0,0) Bragg peak splits, indicating a tetragonal-to-orthorhombic distortion. The mismatch between the a and b lattice parameters appears coincident with the onset of long-range antiferromagnetic order and increases continuously with decreasing temperature, reaching a value of $a/b-1\approx 0.2\%$ at 3.7 K.
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Investigations of the physical properties of the recently discovered[1–5] superconducting rare-earth nickel boride-carbides, RNi_2B_2C (R = rare earth), continue to provide further insight into the interplay between superconductivity and magnetism. The structure of these compounds is tetragonal (space group $I4/mmm$), consisting of RC layers separated by Ni_2B_2 sheets.[3] Superconductivity has been reported not only for the nonmagnetic rare-earth elements, but also for some heavy magnetic rare-earth members, including Tm ($T_C = 10.8$ K),[6] Er ($T_C = 10.5$ K),[7] Ho ($T_C = 8.5$K),[8,9] and, most recently, Dy ($T_C = 6.2$ K).[10] In these latter compounds superconductivity coexists with magnetic ordering over some temperature range. Electronic band-structure calculations[11–14] indicate that these materials are conventional superconductors with a relatively high density of states at the Fermi level.

Throughout the series, the Néel temperature, T_N, scales with the de Gennes factor. This, along with the large variety of magnetic structures observed in neutron and x-ray experiments, is consistent with long-range order of localized magnetic moments coupled via a Ruderman-Kittel-Kasuya-Yosida-type interaction. (For recent overviews, see Refs. 15–17.) The strong anisotropic magnetic behavior found in some members of the family indicates that crystalline electric-field energies (CEF) also play an important role in the formation of the magnetically ordered state.[8,7,18,9,19]

In $ErNi_2B_2C$, superconductivity is observed below $T_C = 10.5$ K.[2,5,7] The onset of long-range antiferromagnetic order below $T_N = 6.0$ K lowers the upper critical field, H_{c2}, especially if the field is applied perpendicular to the (0,0,1) axis. Previous neutron-diffraction experiments, carried out on powder[20] and single-crystal[21] samples, show that $ErNi_2B_2C$ orders in a transverse spin-density wave with modulation wave vector $\mathbf{q}_a = (0.55,0,0)$ and with alignment of the magnetic moments parallel to the (0,1,0) axis of the crystal. The tetragonal symmetry of the crystal also implies the existence of domains with modulation wave vector $\mathbf{q}_b = (0,0.55,0)$ and alignment of the moments along (1,0,0). As the temperature is lowered, higher harmonic satellites were observed to develop,[20,21] which shows that the spin-density wave ''squares up''; the modulation wave vector is approximately independent of temperature.[20,21] A similar magnetic structure was observed in the Gd compound,[22] while $TbNi_2B_2C$ forms a longitudinal spin-density wave with approximately the same wave vector.[23] A complicated structure with two modulation wave vectors, (0.59,0,0) and (0,0,0.92), is found[24–28] in $HoNi_2B_2C$ between 6.0 and 4.7 K, whereas at lower temperatures it orders into a simple antiferromagnetic structure with modulation wave vector (0,0,1).

More recently, small-angle neutron scattering has been used to study the vortex structure of $ErNi_2B_2C$.[29,30] At high fields, these experiments observed a square flux-line lattice, while at low fields the flux lines order in the hexagonal lattice more typically found in type-II superconductors.[30,31] In addition, a significant coupling between the magnetic ordering and the flux lines was observed, as evidenced by rotation of the vortex lines away from the direction of the applied field below the Néel transition, coincident with disordering of the flux-line lattice.[29] These data demonstrate how, in a magnetic superconductor, the vortex lattice structure may be coupled to the magnetic-order parameter.

In this paper, we report the results of x-ray-diffraction measurements on $ErNi_2B_2C$ and demonstrate the existence of an interaction between the crystal structure and the magnetic-order parameter by means of conventional crystalline electric field (CEF) coupling.

Single crystals of $ErNi_2B_2C$ were grown at the Ames Laboratory using a high-temperature flux-growth technique.[8,7] Platelets extracted from the flux were examined by x-ray diffraction and were found to be high-quality single crystals with the (0,0,1) axis perpendicular to their flat surface. Magnetization measurements were performed as a function of temperature and magnetic field, using a Quantum Design superconducting quantum interference device magnetometer on single crystals from a similar batch as those used in the x-ray experiments. The details of these measurements have been reported elsewhere.[7,32] The sample was cut perpendicular to the (1,0,0) direction and the resulting face was mechanically polished to obtain a flat, oriented surface for x-ray diffraction. After polishing, the crystal was annealed at 900 °C in a vacuum of 10^{-7} torr for 36 h. The sample dimensions after polishing were approximately $3\times 1.5\times 0.5$ mm^3.

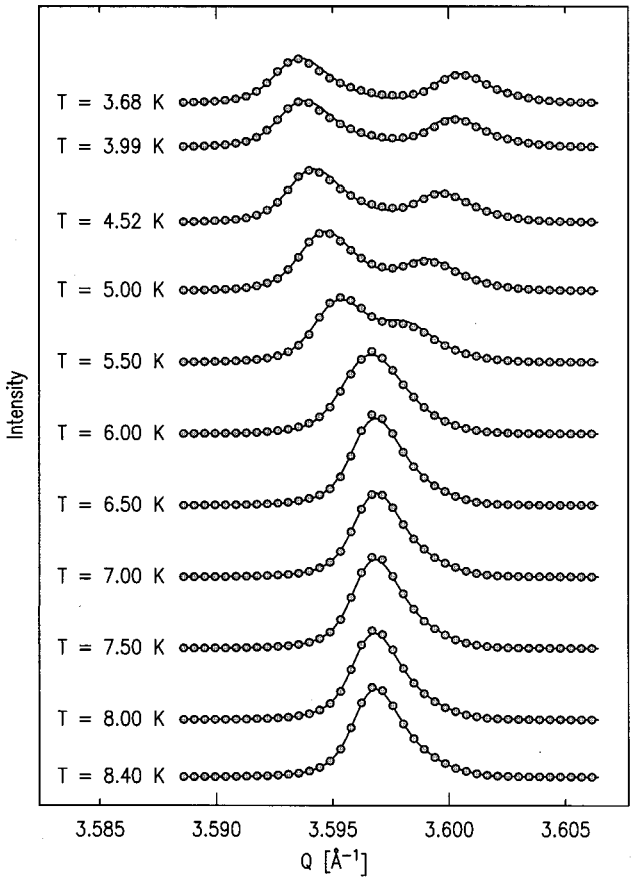

FIG. 1. Representative longitudinal scans of the (2,0,0) Bragg peak at selected temperatures. The lines represent the results of least-squares fits as described in the text. The scan taken at 8.40 K was assumed to be resolution limited and was used as a reference scan for the fitting procedure.

The synchrotron experiments were carried out at the bending magnet beamline X22C of the National Synchrotron Light Source, using a Ge(1,1,1) double bounce monochromator and an asymmetric cut Ge(1,1,1) analyzer. A Ni-coated toroidal focusing mirror upstream of the monochromator was used to eliminate higher harmonics in the incident beam. The sample was mounted on the cold finger of a Heliplex closed-cycle refrigerator (base temperature 3.5 K) so that its $(h,0,l)$ zone was coincident with the vertical scattering plane of the diffractometer. The mosaic spread of the $(h,0,0)$ reflections was characterized by a full width at half maximum (FWHM) of 0.04°. For the measurements of the crystal lattice distortion, the incident photon energy was tuned to 8 keV, well below the Er $L_{1,2,3}$ and the Ni K absorption edges.

Above the Néel temperature, as determined by susceptibility measurements,[7] clearly defined Bragg peaks (h,k,l) with a characteristic width (FWHM) of 0.003 Å^{-1} were observed at $h+k+l=2n$, where n is an integer. The only structure present in these peaks is a slight asymmetry that is also seen in scans through the incident beam. We therefore have taken these peaks to be resolution limited.

Figure 1 shows longitudinal scans through the (2,0,0) Bragg peak for selected temperatures. As the sample is cooled below $\approx$6.3 K, the peak first broadens and then splits, consistent with a tetragonal to orthorhombic phase transition.

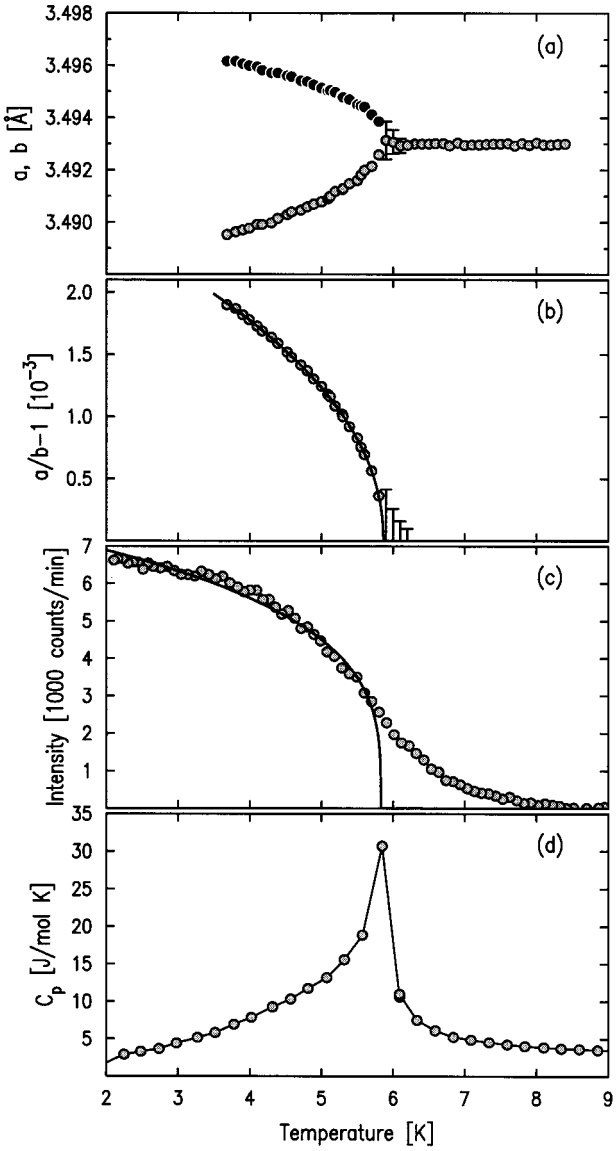

FIG. 2. (a) The a and b lattice parameters extracted from a set of longitudinal scans of the (2,0,0) Bragg peak. (b) The distortion-order parameter, $a/b-1$. The line represents a least-squares fit to a power law, $A(1-T/T_N)^{2\beta}$, as discussed in the text. (c) Intensity of a magnetic Bragg reflection, from Ref. 20. The line represents a least-squares fit to a power law. (d) Specific heat, C_p, in zero applied field, from Ref. 7.

The high- and low-**Q** peaks then correspond to the (0,2,0) and (2,0,0) Bragg peaks of separate domains that are rotated by 90° relative to each other around their (0,0,1) axes. No hysteresis was observed when these measurements were repeated on warming. Despite the relative ease encountered in other rare-earth borocarbides,[22,28,33] we were unable to observe x-ray magnetic scattering at the Er L_3 resonance (8.358 keV) in this material. We believe this is a result of the strong absorption arising from the combination of Ni in the sample and in the mirror, and the presence of the nearby Ni K edge (8.333 keV).

Figure 2 summarizes the temperature dependence of the (2,0,0) Bragg peak as measured on cooling. The lattice parameters, a and b, were extracted by fitting each scan to the convolution of a resolution-limited reference scan (8.40 K)

with two Gaussian line shapes with a fixed width. The results of this procedure are displayed in Fig. 2(a). In the temperature range between 5.9 and 6.3 K, the raw data shows a slight broadening of the (2,0,0) Bragg peak and, within the resolution of this experiment, it is not possible to distinguish two separate peaks. This broadening is therefore represented by the error bars shown in Figs. 2(a) and 2(b). The line in Fig. 2(b) shows the result of fitting the splitting, $a/b-1$, to a power law in the reduced temperature. For the fit shown in the figure, $T_N=5.9\pm0.2$ K. In Fig. 2(c), we show the intensity of a magnetic Bragg reflection as measured by neutron powder diffraction.[20] A least-squares fit to a power law, represented by the line, indicates a ordering temperature $T_N \approx 5.8\pm0.5$ K. While this ordering temperature agrees with the values obtained from the splitting and from magnetization measurements [Fig. 2(d)], it is lower than those reported by Sinha *et al.* ($T_N=6.8$ K, Refs. 20,17), obtained from a fit to a Brillouin function, and by Zarestky *et al.* ($T_N\approx7$ K, Ref. 21). We attribute the differences in T_N to critical scattering observed above the ordering temperature. Finally, in Fig. 2(d), we present the specific heat of $ErNi_2B_2C$ as measured by Cho *et al.* (Ref. 7) in zero applied field. These authors observed a large, λ shaped anomaly with a peak at 5.9 ± 0.2 K, which they associated with the transition of the Er sublattice from paramagnetism to antiferromagnetic order.

To verify that the symmetry at low temperatures is indeed orthorhombic, we studied a sample prepared from crushed single crystals at the high-resolution powder diffractometer H1A of the High Flux Beam Reactor at Brookhaven National Laboratory. A full profile analysis, using the FULLPROF code,[34] was performed on the data taken at $T=3.4$ K. The results are consistent with an orthorhombic distortion as mentioned above. Due to low counting statistics and some strain broadening, however, it was not possible to determine from the refinement if the magnetic modulation wave vector is oriented along the long (a) or the short (b) basal plane axis.

This type of magnetoelastic distortion is common in rare-earth compounds (see, for example, Ref. 35 and references therein). Quantitative calculations of the shape of the magnetic orbitals and the resulting magnetoelastic distortion require precise evaluation of the competing CEF, elastic and magnetic terms in the Hamiltonian,[35] and have not been performed. Nonetheless, we may draw some qualitative conclusions about the other materials in the series.

For the Gd member of the RNi_2B_2C family, which orders with an antiferromagnetic structure very similar to that of the Er compound, we do not expect a magnetoelastic distortion, since the Gd^{3+} ion in its ground state, $^8S_{7/2}$, has spherical symmetry. Indeed, no magnetoelastic effects were observed in an earlier high-resolution x-ray study[22] of this material. In addition, no magnetoelastic effects were observed in high-resolution x-ray experiments on the Sm and Nd compounds.[28,33] In the Sm compound, the moments are aligned parallel to (0,0,1), so that magnetostrictive effects would change the a/c ratio without breaking the crystal symmetry. In $HoNi_2B_2C$ a small magnetostriction was observed as an increase in the mosaic width of nuclear reflections in earlier neutron experiments.[24] For $TbNi_2B_2C$, which orders into a longitudinal spin-density wave state with modulation wave vector (0.55,0,0), we expect a magnetoelastic tetragonal-to-orthorhombic distortion similar to that of the Er compound. High-resolution x-ray-diffraction experiments to probe the structure of this material are planned.

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[1] R. Nagarajan, C. Mazumdar, Z. Hossain, S. K. Dhar, K. V. Gopalakrishnan, L. C. Gupta, C. Godart, B. D. Padalia, and R. Vijayaraghavan, Phys. Rev. Lett. **72**, 274 (1994).

[2] R. J. Cava, H. Takagi, H. W. Zandbergen, J. J. Krajewski, W. F. Peck, Jr., T. Siegrist, B. Batlogg, R. B. van Dover, R. J. Felder, K. Mizuhashi, J. O. Lee, H. Eisaki, and S. Uchida, Nature (London) **367**, 252 (1994).

[3] T. Siegrist, H. W. Zandbergen, R. J. Cava, J. J. Krajewski, and W. F. Peck, Jr., Nature (London) **367**, 254 (1994).

[4] R. Cava, H. Takagi, B. Batlogg, H. W. Zandbergen, J. J. Krajewski, W. F. Peck, Jr., R. B. van Dover, R. J. Felder, T. Siegrist, K. Mizuhashi, J. O. Lee, H. Eisaki, S. A. Cater, and S. Uchida, Nature (London) **367**, 146 (1994).

[5] H. Eisaki, H. Takagi, R. J. Cava, B. Batlogg, J. J. Krajewski, W. F. Peck, Jr., K. Mizuhashi, J. O. Lee, and S. Uchida, Phys. Rev. B **50**, 647 (1994).

[6] B. K. Cho, M. Xu, P. C. Canfield, L. L. Miller, and D. C. Johnston, Phys. Rev. B **52**, 3676 (1995).

[7] B. K. Cho, P. C. Canfield, L. Miller, D. C. Johnston, W. P. Beyermann, and A. Yatskar, Phys. Rev. B **52**, 3684 (1995).

[8] P. C. Canfield, B. K. Cho, D. C. Johnston, D. K. Finnemore, and M. F. Hundley, Physica C **230**, 397 (1994).

[9] K. D. D. Rathnayaka, D. G. Naugle, B. K. Cho, and P. C. Canfield, Phys. Rev. B **53**, 5688 (1996).

[10] B. K. Cho, P. C. Canfield, and D. C. Johnston, Phys. Rev. B **52**, R3844 (1995).

[11] W. E. Pickett and D. J. Singh, Phys. Rev. Lett. **72**, 3702 (1994).

[12] L. F. Mattheiss, Phys. Rev. B **49**, 13 279 (1994).

[13] R. Coehoorn, Physica C **228**, 5671 (1994).

[14] L. F. Mattheiss, T. Siegrist, and R. J. Cava, Solid State Commun. **91**, 587 (1994).

[15] C. Stassis and A. I. Goldman, J. Alloys Compd. **250**, 603 (1997).

[16] J. W. Lynn, J. Alloys Compd. (to be published).

[17] J. W. Lynn, S. Skanthakumar, Q. Huang, S. K. Sinha, Z. Hossain, L. C. Gupta, R. Nagarajan, and C. Godart, Phys. Rev. B **55**, 6584 (1997).

[18] B. K. Cho, Ph.D. thesis, Iowa State University, 1995.

[19] U. Gasser, P. Allenspach, F. Fauth, W. Henggeler, J. Mesot, A. Furrer, S. Rosenkranz, P. Vorderwisch, and M. Buchgeister, Z. Phys. B **101**, 345 (1996).

[20] S. K. Sinha, J. W. Lynn, T. E. Grigereit, Z. Hossain, L. C. Gupta, R. Nagarajan, and C. Godart, Phys. Rev. B **51**, 681 (1995).
[21] J. Zarestky, C. Stassis, A. I. Goldman, P. C. Canfield, P. Dervenagas, B. K. Cho, and D. C. Johnston, Phys. Rev. B **51**, 678 (1995).
[22] C. Detlefs, A. I. Goldman, C. Stassis, P. C. Canfield, B. K. Cho, J. P. Hill, and D. Gibbs, Phys. Rev. B **53**, 6355 (1996).
[23] P. Dervenagas, J. Zarestky, C. Stassis, A. I. Goldman, P. C. Canfield, and B. K. Cho, Phys. Rev. B **53**, 8506 (1996).
[24] A. I. Goldman, C. Stassis, P. C. Canfield, J. Zarestky, P. Dervenagas, B. K. Cho, D. C. Johnston, and B. Sternlieb, Phys. Rev. B **50**, 9668 (1995).
[25] T. E. Grigereit, J. W. Lynn, Q. Huang, A. Santoro, R. J. Cava, J. J. Krajewski, and W. F. Peck, Jr., Phys. Rev. Lett. **73**, 2756 (1994).
[26] T. Vogt, A. I. Goldman, B. Sternlieb, and C. Stassis, Phys. Rev. Lett. **75**, 2628 (1995).
[27] T. Vogt, C. Stassis, A. Goldman, P. Canfield, and B. Cho, Physica B **215**, 159 (1995).
[28] J. P. Hill, B. Sternlieb, D. Gibbs, C. Detlefs, A. I. Goldman, C. Stassis, P. C. Canfield, and B. K. Cho, Phys. Rev. B **53**, 3487 (1996).
[29] U. Yaron, P. L. Gammel, A. P. Ramirez, D. A. Huse, D. J. Bishop, A. I. Goldman, C. Stassis, P. C. Canfield, K. Mortensen, and M. R. Eskildsen, Nature (London) **382**, 236 (1996).
[30] M. R. Eskildsen, P. L. Gammel, B. P. Barber, U. Yaron, A. P. Ramirez, D. A. Huse, D. J. Bishop, C. A. Bolle, C. M. Lieber, S. Oxx, S. Sridhar, N. H. Andersen, K. Mortensen, and P. C. Canfield, Phys. Rev. Lett. **78**, 1968 (1997).
[31] V. G. Kogan, M. Bullock, B. Harmon, P. Miranović, Lj. Dobrosavljević-Grujić, P. L. Gammel, and D. J. Bishop, Phys. Rev. B **55**, R8693 (1997).
[32] P. C. Canfield, S. L Bud'ko, and B. K. Cho, Physica C **262**, 249 (1996).
[33] C. Detlefs, A. H. M. Z. Islam, A. I. Goldman, C. Stassis, P. C. Canfield, J. P. Hill, and D. Gibbs, Phys. Rev. B **55**, 680 (1997).
[34] J. Rodriguez-Carvajal, Physica B **192**, 55 (1993).
[35] P. Morin and D. Schmitt, in *Ferromagnetic materials*, edited by K. H. J. Buschow and E. P. Wohlfarth (North-Holland, Amsterdam, 1990), Vol. 5.